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**Sent:** Friday, October 02, 2020 2:02 PM

To: ngray@dofnw.com Subject: benzyl alcohol

Attachments: 2016-Final BnOH clarification paper\_v2.pdf; LDW AOC4 benzyl alcohol memo\_toEPA\_061020.pdf

Hi Tasya. Attached is the benzyl alcohol paper I mentioned that I learned about last year but is dated 2016. Also attached is LDWG's technical memorandum about why benzyl alcohol is not a COC for the LDW. I'm not saying we shouldn't be looking at benzyl alcohol as a COC for Rhone-Poulenc, especially upland, but like with all the COCs it makes sense to align with the LDW cleanup requirements.

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# Lower Duwamish Waterway Group Port of Seattle / City of Seattle / King County / The Boeing Company

# TECHNICAL MEMORANDUM: SUMMARY OF BENZYL ALCOHOL INFORMATION

#### For submittal to

The U.S. Environmental Protection Agency Region 10

Seattle, WA

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Prepared by:

Wind Ward environmental LLC

in association with



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# **ABBREVIATIONS**

abbreviation definition

AET apparent effects threshold

CERCLA Comprehensive Environmental Response, Compensation, and Liability

Act

COC contaminant of concern
CSO combined sewer overflow

DMMP Dredged Material Management Program
DMMU dredged material management unit

dw dry weight

Ecology Washington State Department of Ecology
EIM Environmental Information Management
EPA U.S. Environmental Protection Agency

ERL effects range-low
ERM effects range-median

ESD Explanation of Significant Differences

FS feasibility study
IQR interquartile range

LDW Lower Duwamish Waterway

LPAH low-molecular-weight polycyclic aromatic hydrocarbon
NOAA National Oceanic and Atmospheric Administration

PAH polycyclic aromatic hydrocarbon

PCB polychlorinated biphenyl PDI pre-design investigation

PSAMP Puget Sound Ambient Monitoring Program

RAL remedial action level RI remedial investigation

RL reporting limit
RM river mile

ROD Record of Decision

SCO sediment cleanup objective

SMS Washington State Sediment Management Standards

SVOC semi-volatile organic compound
USACE U.S. Army Corps of Engineers
UWI Urban Waterways Initiative



WAC Washington Administrative Code

ww wet weight

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# 1 Introduction

This memorandum summarizes technical and policy information about benzyl alcohol to support an Explanation of Significant Differences (ESD) to remove benzyl alcohol as a contaminant of concern (COC) in the Lower Duwamish Waterway (LDW) Record of Decision (ROD).

Design of the sediment remedy for the LDW is underway for the upper reach, with pre-design investigation (PDI) sampling having begun in spring 2020. Therefore, now is the time to establish any corrections/modifications to the remedial action levels (RALs) and cleanup levels that will be considered in the sediment remedial design to dictate actions in the waterway.

As has been recognized for years and acknowledged by several agencies, benzyl alcohol requires special consideration for a number of reasons, as listed below.

- Because of significant improvements in analytical methodology, current analytical
  methods result in more frequently detected benzyl alcohol concentrations above the
  benthic sediment cleanup objective (SCO)<sup>2</sup> than do methods used in the 1980s to
  establish the SCO. Therefore, the current analytical results are not comparable to the SCO.
- Benzyl alcohol is not persistent in the environment.
- In the LDW, benzyl alcohol has been shown to be non-toxic at concentrations at least four times the benthic SCO (which is the same as the cleanup level in the LDW ROD).
- Benzyl alcohol is present in plant-based materials at higher levels than in LDW sediment.
- Benzyl alcohol levels in sediments upstream of the LDW are greater than the benthic SCO.
- Benzyl alcohol levels in storm drain/combined sewer system solids throughout the drainage basin, where detected,<sup>3</sup> are greater than the benthic SCO, including areas with no industrial sources.

Furthermore, benzyl alcohol is not a hazardous substance under Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (Black et al. 2020). Thus, in addition to the

<sup>&</sup>lt;sup>3</sup> See Section 2.5 for detection frequencies and other metrics.



<sup>&</sup>lt;sup>1</sup> See Section 3.2.

<sup>&</sup>lt;sup>2</sup> The marine benthic SCO for benzyl alcohol was established in the Washington State Sediment Management Standards (SMS) (Washington Administrative Code [WAC] 173-204) (see Section 3 of this memo). The marine benthic SCO is the same as the marine sediment quality standard (WAC 173-204-320) and it forms the basis for the cleanup level and RAL for benzyl alcohol presented in the LDW ROD. The cleanup level, as presented in ROD Table 20 (ROD Table 20 is titled *Sediment Cleanup Levels for Ecological (Benthic Invertebrate) COCs for RAO3*), is equal to the benthic SCO, whereas the RAL is either the same as or two times the benthic SCO, depending on the recovery category of the location within the LDW (see ROD Table 28; ROD Table 28 is titled *Remedial Action Levels, ENR Upper Limits, and Areas and Depths of Application*).

legal basis, a strong technical case supports the recommendation to remove benzyl alcohol as a COC in the LDW ROD.

# 2 Technical Information

This section provides an overview of the chemical characteristics of benzyl alcohol; changes to laboratory analysis methods that have improved the quality of analytical results; a summary of LDW sediment and bioassay results; and a summary of benzyl alcohol concentrations in upstream sediments, LDW storm drain /combined sewer system solids, and Puget Sound sediments.

# 2.1 Chemical Characteristics

Benzyl alcohol is readily biodegradable, with 94% degradation measured in a standard 28-day aqueous test conducted under aerobic conditions (NIH 2019), and thus it is not persistent in the aquatic environment. Benzyl alcohol has a log octanol-water partition coefficient ( $K_{ow}$ ) range of 1.00 to 1.16 (EPA 1989; Montgomery 2000). Chemicals with (log  $K_{ow}$  < 2.7) generally have low sorption to solids, low bioaccumulation potential, high biodegradation rates, and high solubility (Fourie and Fox 2016) .

# 2.2 Analytical Methods and LDW Data

Benzyl alcohol was rarely detected in sediment collected in Washington State, including in the LDW, prior to 2010 (Fourie and Fox 2016). In the LDW remedial investigation/feasibility study (RI/FS) dataset (Windward 2010; AECOM 2012), benzyl alcohol was rarely detected in sediment samples with reporting limits (RLs) that ranged from 3.1 to 4,200  $\mu$ g/kg, with a mean RL of 93  $\mu$ g/kg. RLs are sample specific and are affected by sample dilution; the higher RL values reflect samples that were diluted in order to get target semi-volatile organic compound (SVOC) concentrations within calibration ranges.

There were very few detected results in the RI/FS dataset that exceeded the benzyl alcohol benthic SCO (Table 1, Figure 1). However, sediment investigations conducted since 2010 have reported greater detection frequencies of benzyl alcohol and greater numbers of concentrations exceeding the benthic SCO.

**Table 1 Summary of LDW-wide Surface Sediment Benzyl Alcohol Data** 

Date Range	No. of Sediment Samples	Detection Frequency	Conc. Range µg/kg dw	Mean Conc.¹ μg/kg dw	RL Range µg/kg dw	No. of Non-detect Samples with RLs > Benthic SCO	No. of Samples with Detected Benthic SCO Exceedances	Detected Benthic SCO Exceedance Frequency		
RI/FS D		Trequency	μg/ kg an	u ii	μg/kg uti	500	Exceedinees	rrequency		
1990– 1994	55	0%	-	-	13 - 77	3	0	0%		
1995– 1999	505	0.6%	23 - 48	33	18 - 690	99	0	0%		
2000– 2004	90	4.4%	8.2 - 72	29	9.2 - 500	9	1	1.1%		
2005– 2009	294	8.2%	20 - 670	110	3.1 - 4,200	23	16	5.4%		
Post-FS	Post-FS Dataset									
2010– 2014	495	64%	2.5 - 17,000	210	2.2 - 250	14	221	45%		
2015– 2018	140	40%	4.4 - 600	75	18 - 59.8	4	21	15%		

#### Notes:

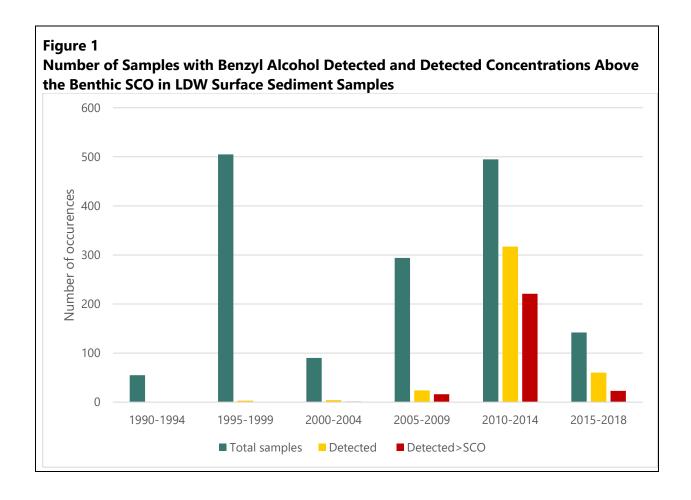
1. Mean calculated based on detected concentrations only.

dw: dry weight FS: feasibility study

LDW: Lower Duwamish Waterway

RI: remedial investigation RL: reporting limit

SCO: sediment cleanup objective



In 2016, the U.S. Army Corps of Engineers (USACE) reviewed the changes in benzyl alcohol concentrations in Washington State on behalf of the Dredged Material Management Program (DMMP) and concluded that the most likely cause of the dramatic increase in benzyl alcohol detections and concentrations since 2010 was changes in the analytical methods used for the analysis of SVOCs (Fourie and Fox 2016). The changes in analytical methods included improvements in sample extraction methods, extract cleanup methods, and analytical technology, including chromatographic equipment and instrument conditions, such as injection port temperatures (EPA 2018).

Benzyl alcohol is quantified as an SVOC using U.S. Environmental Protection Agency (EPA) method 8270. This method was developed for the analysis of non-polar organic compounds, such as polycyclic aromatic hydrocarbons (PAHs) and phthalates. Benzyl alcohol is more chemically reactive than these non-polar compounds, and laboratories have historically had difficulty with benzyl alcohol recoveries due to issues with sample extraction and chromatographic interferences. Specifically, benzyl alcohol is more polar than the other SVOC analytes and has a strong tendency to react with high-molecular-weight humic materials present in a sample, thereby reducing target analyte recovery. This results in a low bias in the reported

concentrations because a significant fraction of the benzyl alcohol is lost in the analytical process.

In the 1990s, the standard sediment sample mass for SVOC analysis was larger (60 to 100 g wet weight [ww]) than the mass required by current extraction protocols (20 to 30 g ww). The larger sediment masses were necessary to achieve the required sensitivity for target analytes. However, the larger sample sizes also resulted in high levels of high-molecular-weight humic materials and other reactive materials. The presence of these interfering compounds required additional cleanup steps that removed both the interfering compounds and the benzyl alcohol.

In order to increase efficiency and sensitivity, laboratories have developed protocols that enable them to reduce the sediment mass required for analysis. Less mass reduces the presence of humic materials that can cause matrix interferences in the sample extract. Fewer interferences reduces the need for post-extraction cleanup steps and improves the chromatographic performance of the sample. The improvements in laboratory protocols have resulted in increased detections and concentrations of benzyl alcohol (Fourie and Fox 2016).

Because the analytical method and equipment changes are responsible for the increased benzyl alcohol detections and concentrations, the 1986 sediment data used to set the benthic SCO are biased low relative to the results currently being reported. Therefore, an SCO exceedance based on current analytical methods is not directly comparable to an SCO exceedance in samples collected prior to the analytical method changes. As a result, the benzyl alcohol concentration at which toxicity may occur would be greater than the SCO when samples are analyzed with the updated analytical methods. The use of older methods is not a viable option, as their sensitivity is not sufficient to meet the SCO as demonstrated by the large number of non-detected results with RLs greater than the SCO in the LDW RI/FS dataset.

Map 1 shows post-2010 benzyl alcohol chemistry data for LDW surface sediment, and Map 2 presents both RI/FS and post-FS data relative to the LDW ROD-specified RALs (equal to benthic SCO or two times benthic SCO depending on recovery category designation). Table 2 summarizes the RAL exceedances and shows much higher detection frequencies and number of locations with RAL exceedances in the post-FS dataset. For reference, benzyl alcohol data are summarized in an Excel file in Appendix A.

Table 2
Summary of Benzyl Alcohol RAL Exceedances in Surface Sediment in the LDW

Dataset	No. of Locations <sup>1</sup> with Detected Benzyl Alcohol RAL Exceedances	No. of Locations <sup>1</sup> with Only Detected Benzyl Alcohol RAL Exceedances		
RI/FS	7	1		
Post-FS	163	112		

#### Notes:

1. Numbers of locations do not include locations that have been dredged or are within EAAs because EAAs have been remediated. In addition, locations were counted more than once if they were monitoring locations with RAL exceedances outside of EAAs.

EAA: Early Action Area FS: feasibility study

LDW: Lower Duwamish Waterway

RAL: remedial action level RI: remedial investigation

Sediment data within the LDW were reviewed to determine if temporal variability or trends could be assessed. Insufficient data are available since 2010 to clearly demonstrate temporal trends in benzyl alcohol in the absence of information on other variables, because few locations have been sampled more than once for benzyl alcohol.

# 2.3 LDW Sediment Bioassay Data

SMS include both chemical and biological criteria with the biological criteria being an override when chemical criteria are exceeded (Washington Administrative Code [WAC] 173-204-310). In the LDW, bioassays have been conducted for 20 surface sediment samples with post-2010 chemistry data (Map 3). All of these samples were collected in 2011 as part of a sediment characterization study that occurred in the vicinity of the former Rhone-Poulenc facility (Cardno Entrix 2012); all 20 samples passed the SMS biological criteria. The highest benzyl alcohol concentration in surface sediment tested (without other SCO-exceeding chemicals) passing all three bioassays was 260  $\mu$ g/kg (Table 3). This concentration is more than four times greater than the benthic SCO of 57  $\mu$ g/kg.

In addition to the 20 surface sediment samples for which bioassays were conducted, 19 subsurface composite sediment samples collected for a different project were submitted for bioassay testing for dredge disposal decisions. The data for the subsurface samples with bioassay results are provided in Table 3. The subsurface composites samples were collected by USACE to characterize shoal material throughout the LDW (USACE 2013) and dredge material in the navigation channel between river mile (RM) 4.05 and RM 4.65 (USACE et al. 2018) (Map 3).<sup>4</sup>

<sup>&</sup>lt;sup>4</sup> Only the shoal characterization locations are shown on Map 3.

**Table 3 Bioassay Results for Surface Sediment Samples Collected in the LDW** 

_			•							
Sample	Benzyl Alcohol Conc. (µg/kg)	Benzyl Alcohol Conc. > Benthic SCO?	Additional Benthic SCO Exceedance? <sup>1</sup>	Amphipod	Larval	Polychaete	Overall (SMS Result) <sup>2</sup>			
Surface Sediment										
IT1	14	no	no	pass	pass	pass	pass			
IT3	19	no	no	pass	pass	pass	pass			
IT7	43	no	no	pass	pass	pass	pass			
IT5	49	no	no	pass	pass	pass	pass			
IT11	65	yes	no	pass	pass	pass	pass			
BKG-2	68	yes	yes - SVOC³	pass	pass	pass	pass			
IT13	87	yes	yes - PCBs	pass	pass	pass	pass			
IT8	93	yes	no	pass	pass	pass	pass			
IT6	96	yes	no	pass	pass	pass	pass			
IT14	100	yes	no	pass	pass	pass	pass			
BKG-6	110	yes	no	pass	pass	pass	pass			
IT9	110	yes	no	pass	pass	pass	pass			
IT10	110	yes	no	pass	pass	pass	pass			
BKG-1	120	yes	no	pass	pass	pass	pass			
IT2	120	yes	no	pass	pass	pass	pass			
BKG-3	170	yes	no	pass	pass	pass	pass			
BKG-5	180	yes	no	pass	pass	pass	pass			
IT12	220	yes	no	pass	pass	pass	pass			
BKG-4	260	yes	no	pass	pass	pass	pass			
IT4	260	yes	no	pass	pass	pass	pass			
Subsurfac	e sediment									
DMMU 4	60	yes	no	pass	pass	pass	pass			
DMMU 12	66	yes	no	pass	pass	pass	pass			
DMMU 17	68	yes	no	pass	pass	pass	pass			
DMMU 11	72	yes	no	pass	fail (SCO)	pass	pass			
DMMU 5	82	yes	no	pass	pass	pass	pass			

Sample	Benzyl Alcohol Conc. (µg/kg)	Benzyl Alcohol Conc. > Benthic SCO?	Additional Benthic SCO Exceedance? <sup>1</sup>	Amphipod	Larval	Polychaete	Overall (SMS Result) <sup>2</sup>
LDW07 2-4C2	84	yes	no	pass	fail (SCO)	pass	pass
LDW08 0-4C1	84	yes	no	pass	fail (SCO)	pass	pass
DMMU 7	86	yes	yes – PCBs <sup>4</sup>	pass	fail (SCO)	pass	pass
DMMU 10	91	yes	no	pass	pass	pass	pass
LDW13 2-7.2C2	100	yes	no	pass	fail (CSL)	pass	fail
LDW09 0-2.1C	120	yes	yes – PCBs	pass	fail (SCO)	pass	pass
LDW11 0-3.7C	130	yes	no	pass	fail (SCO)	pass	pass
LDW16 0-2.5C	130	yes	no	pass	fail (CSL)	pass	fail
DMMU 8	140	yes	no	pass	pass	pass	pass
DMMU 9	140	yes	no	pass	pass	pass	pass
LDW17 0-3.5C	160	yes	yes - PCBs	pass	fail (CSL)	pass	fail
DMMU 6	200	yes	no	pass	fail (SCO)	pass	pass
LDW07 0-2C1	200	yes	no	pass	fail (SCO)	pass	pass
LDW18 0-2.8C	290	yes	no	pass	fail (SCO)	pass	pass

## Notes:

Source: Cardno Entrix (2012) and Fourie and Fox (2016)

- 1. Benthic SCO exceedances for chemicals other than benzyl alcohol.
- 2. SMS biological criteria are described in WAC 173-204-562.
- 3. Sample also exceeded the benthic SCO for 2,4-dimethylphenol, dibenzofuran, five individual PAHs, and total LPAH.
- 4. Primary sample had PCB concentration below the benthic SCO; field duplicate sample PCB concentration exceeded the benthic SCO.

CSL: cleanup screening level

DMMU: dredged material management unit

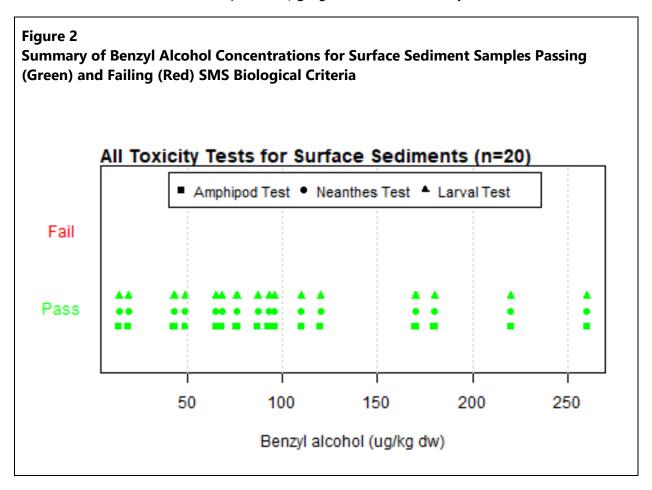
LDW: Lower Duwamish Waterway

LPAH: low-molecular-weight polycyclic aromatic hydrocarbon

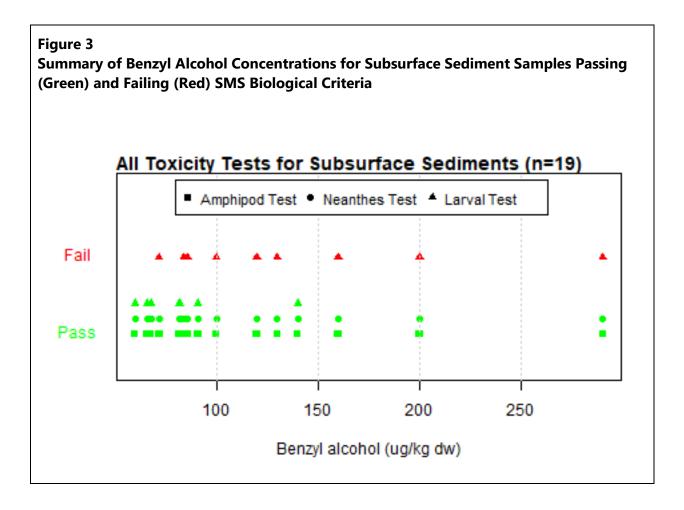
PAH: polycyclic aromatic hydrocarbon

PCB: polychlorinated biphenyl SCO: sediment cleanup objective SMS: Sediment Management Standard SVOC: semi-volatile organic compounds WAC: Washington Administrative Code

The benthic SCO applies to the biologically active zone in surface sediments. The bioassay results for surface sediment are shown graphically in Figure 2, demonstrating that no toxicity was observed at concentrations up to  $260 \mu g/kg$  for all three bioassays.



In addition, for informational purposes, the bioassay results for the subsurface sediment are shown in Figure 3. No amphipod or neanthes toxicity was observed at concentrations up to 290  $\mu$ g/kg, whereas the oyster larval test had failures (9 failures out of 19 tests). The oyster larval test failures occurred in only subsurface sediments and were likely associated with physical and chemical characteristics of the subsurface sediment matrix (e.g., clay fraction, changing redox potential).



The bioassay results demonstrate that the benzyl alcohol SCO of 57  $\mu$ g/kg is not predictive of toxicity in these sediments. If this dataset, which reflects current analytical methods and bioassays, was used to calculate an apparent effects threshold (AET)<sup>5</sup> for benzyl alcohol, that value would be at least 260  $\mu$ g/kg.

## 2.4 Source Information

Benzyl alcohol is an aromatic organic alcohol that is present in a wide variety of natural substances, including leaf litter, small woody debris, and other herbaceous material of terrestrial origin (Fourie and Fox 2016). For example, as described in Fourie and Fox (2016), the benzyl alcohol concentrations in fully and partially aged "dark fines" (i.e., leaves, branches, bark and stems from the forest floor) used in the Boeing Plant 2 restoration project were 3,910 and  $450 \,\mu g/kg$ , respectively (Floyd|Snider 2013). Naturally occurring benzyl alcohol is also found in

<sup>&</sup>lt;sup>5</sup> The AET is the underlying basis for establishment of the benthic SCO.

 $<sup>^6</sup>$  Benzoic acid (a breakdown product of benzyl alcohol) concentrations were also elevated: 5,600 and 3,630  $\mu$ g/kg for the fully aged and partially aged stockpiles, respectively.

some edible fruits (up to 5,000  $\mu$ g/kg) and in green and black teas (1,000 to 30,000 and 1,000 to 15,000  $\mu$ g/kg, respectively) (Fourie and Fox 2016).

In addition, there are potential industrial and domestic sources of benzyl alcohol to the LDW. Benzyl alcohol is produced industrially for use as a solvent, a preservative, and feedstock for the manufacture of other chemicals. It can be used in inks, paints, epoxy resins, paint strippers, soap, perfume, and cosmetics, and it can be added to some foods and beverages as a carrier solvent for flavoring substances at concentrations up to  $400,000 \,\mu\text{g/kg}$  (Fourie and Fox 2016). In 2009, the U.S. Food and Drug Administration approved a 5% solution (50,000,000  $\mu\text{g/kg}$ ) for the treatment of head lice in patients six months of age and older (CDC 2020).

Based on a study conducted by the King County Industrial Waste Program, samples were collected in 2006 from industrial users of the King County sewerage system, with an emphasis on users located within LDW combined sewer overflow (CSO) basins (King County 2008). This study identified industrial users with benzyl alcohol concentrations in their sewer discharges and further categorized those users with respect to concentration (i.e., > 250  $\mu$ g/L, > 100  $\mu$ g/L, and < 100  $\mu$ g/L). Laundry-linen was the only industry in the highest concentration category. Laundry-linen was also in the mid-concentration category, as were centralized waste treatment and paint manufacturing. Twenty additional industrial categories were identified with < 100  $\mu$ g/L in discharges, including metal recycling and finishing, fueling facilities, and barrel cleaning.

Users of benzyl alcohol in industrial and commercial activities are managed through industrial waste discharge permits. These users are required to discharge to the sewer and not to the LDW. Thus, the only potential pathway to the LDW is through CSOs, which discharge infrequently and during storms, when discharge is diluted by large volumes of stormwater. The average concentration in CSOs from the LDW and East Waterway<sup>7</sup> has been 2  $\mu$ g/L (King County 2011). Because benzyl alcohol is highly soluble, it would not be expected to partition significantly to solids that might settle in the LDW.

Some questions have been raised regarding the area near the former Rhone-Poulenc facility at Slip 6, where toluene contamination and vanillin production have been documented. Benzyl alcohol and benzoic acid are transient intermediate by-products of toluene oxidation by bacteria under anaerobic conditions in the laboratory (Altenschmidt and Fuchs 1992). Thus, it is possible that the benzyl alcohol and benzoic acid detections in this area of the LDW are related to toluene releases; however, this pathway has not been evaluated. As discussed in Section 2.2, bioassays in this area have confirmed that its sediments (with benzyl alcohol concentrations ranging from 14 to 260  $\mu$ g /kg) are not toxic to benthic invertebrates.

<sup>&</sup>lt;sup>7</sup> The King County study included both CSO water samples and water samples from within the combined system, which are collected when flows from stormwater inputs are high enough to potentially result in CSO discharges.



In the Trotsky area (RM 2.2)<sup>8</sup> of the LDW, concentrations of benzyl alcohol ranged from 7.3 J to 17,000  $\mu$ g/kg. Barrel-cleaning operations in this area have occurred, potentially contributing benzyl alcohol and other COCs. This area will be remediated regardless of benzyl alcohol concentrations; it has many contaminants with concentrations much greater than their RALs.

# 2.5 Upstream and Storm Drain/Combined Sewer System Solids Data

This section presents upstream sediment data and storm drain/combined sewer system solids data for benzyl alcohol. As discussed in Section 5.1 of the FS (AECOM 2012), more than 99% of the incoming sediment load to the LDW originates from the Green/Duwamish River (upstream); less than 1% solids enters the LDW from lateral sources (which include storm drain/combine sewer system inputs). About 50% of the incoming solids deposit within the LDW. Therefore, the concentrations associated with incoming sediment, especially upstream sediment, are important with respect to concentration expectations in surface sediment within the LDW.

Using the updated analytical methods, the mean and median benzyl alcohol concentrations in upstream bedded and suspended sediment<sup>9</sup> and storm drain/ combined sewer system solids throughout the LDW drainage basins are greater than the RALs and cleanup levels for benzyl alcohol (Table 4, Figure 4). With a few exceptions, <sup>10</sup> these concentrations are all less than those in aged "dark fines" (i.e., leaves, branches, and bark and stems from the forest floor), as quantified in the Boeing Plant 2 restoration project discussed in Section 2.4. In combination with observations of vegetative matter in storm drains, this comparison suggests that vegetative matter is an important source of benzyl alcohol. CERCLA policy generally does not support a cleanup level that is less than concentrations entering a site from upstream (EPA 2002). The only identified upstream industrial or commercial sources discharge to the sanitary sewer (not a combined sewer system), which has no releases to the Green/Duwamish River or tributaries, and there are no CSOs that discharge upstream of the LDW.

<sup>&</sup>lt;sup>8</sup> The Trotsky area was one of the original early action areas based on PCB contamination levels (Windward 2003).

<sup>&</sup>lt;sup>9</sup> Benzoic acid also had elevated concentrations upstream; it ranged from 110 to 3,200  $\mu$ g/kg in suspended sediments with a mean of 1,257  $\mu$ g/kg (Conn et al. 2018a).

<sup>&</sup>lt;sup>10</sup> Samples with benzyl alcohol concentrations greater than the concentration in fully aged dark fines (3,910 μg/kg) include one catch basin solid sample from a Seattle Public Utilities storm drain (5,760 μg/kg) and three samples in Environmental Information Management (EIM)-reported solids samples (one from an oil-water separator at Industrial Containers near Trotsky [63,000 μg/kg], one near Glacier [53,000 μg/kg], and one from a catch basin sampled by Waste Management [7,000 μg/kg]).

Table 4
Benzyl Alcohol Concentrations Reported Since 2010 in LDW Sediment, LDW Storm Drain/
Combined Sewer System Solids, and Bedded and Suspended Sediment Upstream in the
Green/Duwamish River

		Detection	Benzyl Alc	Standard		
Dataset	n	Frequency	Range	Median <sup>1</sup>	Mean <sup>1</sup>	Deviation
LDW surface sediment	635	59%	2.5–17,000 <sup>2</sup>	110	189	883
Storm drain solids <sup>3</sup>	124	44%	33–5,760	370	689	1,050
King County Combined sewer system solids <sup>4</sup>	21	10%	157–411	284	284	180
Additional source solids reported in EIM <sup>5</sup>	86	34%	14–63,000	210	4,740	14,900
Upstream bedded sediment <sup>6</sup>	15	93%	130–570	205	280	162
Upstream suspended sediment <sup>5</sup>	25	76%	54–1,100	600	639	287

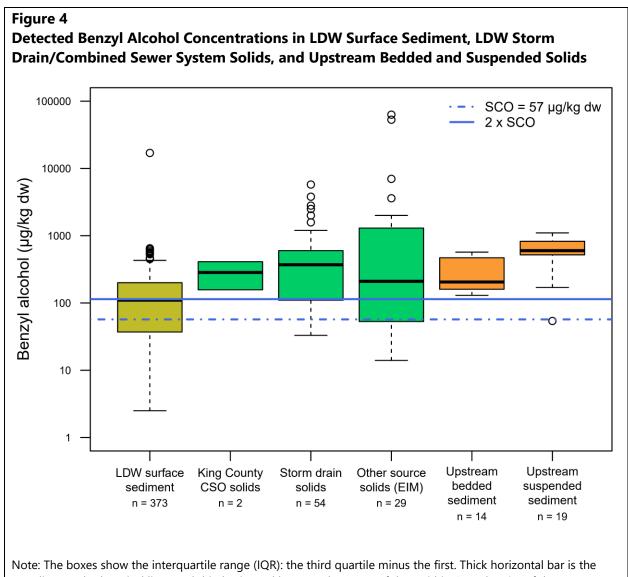
#### Notes:

- 1. Median and mean calculated based on detected concentrations only.
- 2. The sample with the highest concentration was collected in Trotsky Inlet. The next highest concentration was 650 µg/kg, which was in a sample collected as part of the Ecology outfall study in 2011.
- 3. The storm drain dataset includes sediment trap, in-line grab, and catch basin grab samples collected by King County and Seattle Public Utilities from 2010 to 2017.
- 4. The CSO dataset includes King County source tracing solids collected from 2011 to 2016 as in-line grab and sediment trap samples.
- 5. Additional solids data were compiled from EIM and other sources and incorporate data collected from 2010 to 2016, comprising a wide range of sample types including catch basins, treatment systems, manholes, and oil-water separators.
- 6. Source of upstream data: Conn et al. (2018b), Conn et al. (2015), and Conn and Black (2014).

CSO: combined sewer overflow

Ecology: Washington State Department of Ecology EIM: Environmental Information Management

LDW: Lower Duwamish Waterway



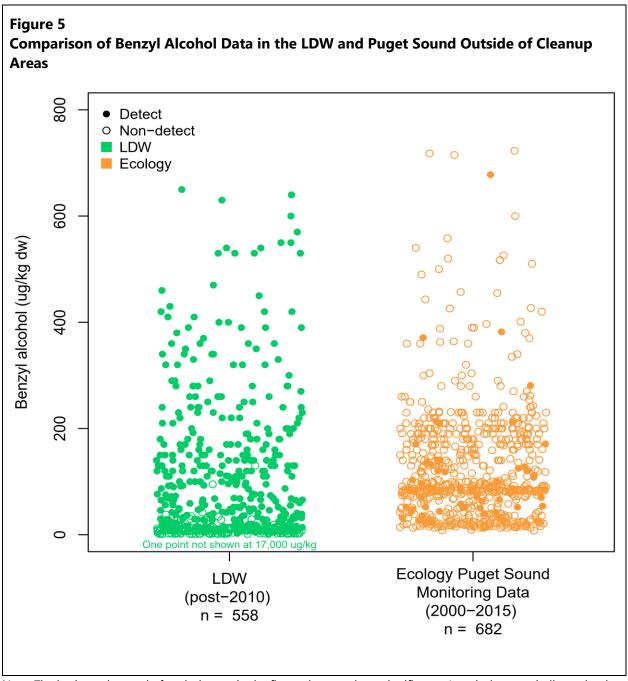
Note: The boxes show the interquartile range (IQR): the third quartile minus the first. Thick horizontal bar is the median. Dashed vertical lines and thin horizontal bars are the range of data within 1.5 x the IQR of the nearest quartile. Data that fall outside the thin horizontal bars are shown as open circles.

# 2.6 Puget Sound Data

The Washington State Department of Ecology's (Ecology's) EIM database was searched for benzyl alcohol sediment data for Puget Sound. The greatest quantity of data was associated with Puget Sound monitoring datasets, specifically from the Ecology Urban Waterways Initiative (UWI) and Puget Sound Ecosystem Monitoring Program (PSEMP). Benzyl alcohol was generally not detected in the monitoring datasets with RLs up to 723  $\mu$ g/kg (Figure 5). RLs associated with these programs were often high and variable, because the analytical methodology had not been updated from the methods used in the 1980s. These programs did not update the methods for

<sup>&</sup>lt;sup>11</sup> Formerly Puget Sound Ambient Monitoring Program (PSAMP).

benzyl alcohol to enable trend analysis using consistent methodology (McGroddy 2020). Use of the older method in the monitoring programs makes comparison to LDW concentrations (using updated methods) difficult. The ranges of the detected data are similar, but there are many non-detects in the monitoring dataset throughout this range (Figure 5).



Note: The horizontal spread of each dataset in the figure does not have significance (e.g., it does not indicate the date of collection). It is merely a presentation style that allows a clear representation of each dataset.

The UWI sediment sample with the highest detected concentration of benzyl alcohol (678  $\mu$ g/kg) was collected from the East Waterway in Seattle in 2007. This sample was not toxic based on the sea urchin fertilization bioassay test conducted (Fourie and Fox 2016). This sediment sample also had concentrations of other chemicals above the benthic SCO, including phthalates and polychlorinated biphenyls (PCBs).

In general, benzyl alcohol data from 2000 to 2015 from these monitoring programs are difficult to interpret due to the continued use of the1980s SVOCs method during this period (Striplin 1988). This older method resulted in RLs for benzyl alcohol that were highly variable and often greater than the benthic SCO. In 2015, benzyl alcohol was removed from the UWI and PSEMP monitoring programs analyte list; it is no longer monitored because it is not a priority chemical for these programs' assessment of trends (Ecology 2016). Specifically, benzyl alcohol, benzoic acid, 2,4-dimethylphenol, phenol, 2-methylphenol, and 4-methylphenol were dropped from PSEMP and UWI monitoring because the base/neutral/acid analytical method was not optimal for these chemicals and the laboratory results were highly variable.

# 3 Policy

This section describes how the benthic SCO for benzyl alcohol, which is also the cleanup level and RAL documented in the LDW ROD, was developed. It also provides an overview of how benzyl alcohol is being addressed in other sediment programs.

# 3.1 Development of the Benthic SCO

The benthic SCO is based on the lowest AET value (57  $\mu$ g/kg for benzyl alcohol). In turn, the benzyl alcohol cleanup level (ROD Table 20) and RALs (ROD Table 28) are based on the benthic SCO. The AET for benzyl alcohol was established in 1986 based on the AET for the Microtox® bioassay. The dataset used to establish the AET consisted of 55 samples collected in 1984 for the Commencement Bay RI (Tetra Tech 1985); the detection frequency of benzyl alcohol in that dataset was 53%. Therefore, the AET was based on 29 samples with detected benzyl alcohol concentrations ranging from 10 to 140  $\mu$ g/kg. This dataset had unusually low detection limits for benzyl alcohol for that time (10  $\mu$ g/kg), which would be difficult to achieve even using standard EPA methods in 2020.<sup>12</sup>

Uncertainty associated with the derivation of AETs for compounds such as benzyl alcohol was discussed in the 1988 predictability evaluation of the 1986 Puget Sound AETs (Barrick et al. 1988). Specifically, the chemical group including benzyl alcohol did not "uniquely account for predicted impacts in either the amphipod or benthic infauna AET." In addition, the analytical difficulties in achieving RLs below the AET for benzoic acid and benzyl alcohol were noted. As indicated in Barrick et al. (1988), given the fact that these AETs did not improve the ability to predict sediment toxicity, the fact that benzyl alcohol was commonly reported as non-detected with RLs greater than the AET was not identified as problematic in implementing the AETs as standards at the time.

# 3.2 Other Sediment Programs

Fourie and Fox (2016) also surveyed other state and federal programs in their clarification paper on benzyl alcohol. They found that of the four states with marine sediment quality criteria (Alaska, California, New York, and Florida), none include a screening level for benzyl alcohol. Furthermore, the National Oceanic and Atmospheric Administration (NOAA) effects ranges-low (ERLs) and effects ranges-median (ERMs) sediment quality guidelines do not include values for benzyl alcohol (Long et al. 1995).

Within Washington State, the Seattle District DMMP agencies (Ecology, USACE, EPA, and Washington Department of Natural Resources) have been using best professional judgement in in an increasing number of projects to determine whether to test for benzyl alcohol toxicity.

<sup>&</sup>lt;sup>12</sup> Currently, ARI reports to 19 µg/kg.



As a result, and having stated that they "do not believe that benzyl alcohol is a chemical of significant concern at the concentrations found in many dredging projects" using current analytical methods (Fourie and Fox 2016), the 2016 DMMP clarification paper recommends a re-evaluation of the benzyl alcohol guidelines. Recent sediment samples from the LDW upper reach have had concentrations of benzyl alcohol similar to those discussed in DMMP's clarification paper (i.e., DMMP sediment samples that passed bioassay criteria had concentrations between 60 and 290  $\mu$ g/kg).

It is also worth noting that there is no benzyl alcohol cleanup level for freshwater sediment in Washington State (WAC 173-204-563); insufficient data are available. Also, there are no state or national water quality criteria for benzyl alcohol.

In addition, EPA has not considered benzyl alcohol as meeting any of the specific criteria for designation as a hazardous substance under CERCLA or a hazardous waste under RCRA.

# 4 Conclusions

This memorandum provides the technical and policy considerations supporting the removal of benzyl alcohol as a COC in the LDW ROD.

This conclusion is supported by chemical and toxicity data from the LDW and elsewhere. In particular, median and mean benzyl alcohol concentrations in upstream sediment entering the LDW are greater than the ROD cleanup level and RALs, and benzyl alcohol in the LDW has been shown to be non-toxic at concentrations at least four times greater than the cleanup level (which is equal to the benthic SCO). In addition, benzyl alcohol is readily biodegradable and thus it is not persistent in the aquatic environment.

Because the analytical method changes are responsible for increased benzyl alcohol detections and concentrations, the 1986 sediment data used to set the benthic SCO are biased low relative to the results currently being reported. Therefore, an SCO exceedance based on current analytical methods is not directly comparable to an SCO exceedance in samples collected prior to the analytical method changes. As a result, the benzyl alcohol concentration at which toxicity may occur would be greater than the SCO when samples are analyzed with the updated analytical methods.

In addition, benzyl alcohol, which has natural, industrial, and commercial sources, is present in natural materials (e.g., mulch) at levels much higher than those in LDW sediment.

Other national programs do not have water or sediment criteria for benzyl alcohol, it is no longer an analyte in Puget Sound monitoring programs, and is increasingly the subject of best professional judgement decisions by the DMMP. Benzyl alcohol does not constitute a hazardous substance under CERCLA.

Thus, in addition to legal reasons, a strong technical case supports the recommendation to eliminate the cleanup level and RAL for benzyl alcohol from the LDW ROD.

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# Appendix A Benzyl Alcohol Sediment and Storm Drain/Combined Sewer System Solids Data

See associated Excel file.

# Revised Evaluation Guidelines for Benzyl Alcohol in Marine Sediments

Prepared by Heather Whitney Fourie (U.S. Army Corps of Engineers) and David Fox (U.S. Army Corps of Engineers) for the DMMP agencies.

# Introduction

Benzyl alcohol is one of the standard Dredged Material Management Program (DMMP) chemicals of concern (COCs) required to be analyzed for dredging projects in marine waters. It has a screening level (SL) of 57 ug/kg and a maximum level (ML) of 870 ug/kg (DMMP, 2015b).

The DMMP evaluation guidelines require toxicity testing if one or more COC exceeds its SL. Toxicity testing consists of a suite of three bioassays: a 10-day amphipod mortality test; 48-hr bivalve or echinoderm larval development test; and a 20-day juvenile infaunal mortality and growth test using *Neanthes arenaceodentata*.

#### Problem Identification

Since around 2011, benzyl alcohol has been much more frequently detected in dredged material characterization studies than in the years prior (1989-2010). More importantly, benzyl alcohol has been the only COC to exceed its SL in several recent DMMP projects, including the Duwamish Turning Basin and Navigation Channel O&M (2011), Snohomish Navigation Channel O&M (2012), Shelter Bay Marina (2014a), La Connor Marina (2014b), and Bellingham Cold Storage (2015a). Under the current DMMP guidance, biological testing of sediments is required for even a single exceedance of a marine SL. However, unlike other anthropogenic contaminants such as PCBs and organochlorine pesticides, benzyl alcohol has both industrial and natural sources, and has long been suspected of being associated with leaf litter, small woody debris or other herbaceous or ligneous material of terrestrial origin. This led the DMMP agencies to apply best professional judgment (BPJ) to eliminate the requirement for bioassays for four of the five projects listed above. Concurrent bioassays were conducted on all samples from the Duwamish O&M project, so use of BPJ was not necessary in that case.

Best professional judgment is used on a case-by-case basis to address analytical problems, ambiguous data or other project-specific issues that arise during dredged material characterization. However, the number of cases in which benzyl alcohol was the only COC exceeding SL reached a point where the DMMP agencies determined that a more rigorous evaluation was needed to validate the use of BPJ.

#### **Technical Evaluation**

Seattle District conducted a multifaceted technical evaluation on behalf of the DMMP agencies, including an investigation into the increasing number of benzyl alcohol detections; a review of the sources of benzyl alcohol; research into its biodegradability; mapping of its distribution; a review of disposal site monitoring data; an evaluation of its toxicity; and a review of the origins of its regulation in the State of Washington.

## Why the Increase in Detections of Benzyl Alcohol?

#### Data trend

Figure 1 displays the number of Dredged Material Management Units (DMMUs) with detects and non-detects of benzyl alcohol that exceeded the current SL of 57 ug/kg by biennial report year. Prior to 2005, benzyl alcohol was frequently reported as a non-detect above the SL in DMMP projects, but was only detected once above the SL. After 2005, the number of benzyl alcohol non-detects that exceed the SL drops off dramatically, and a significant increase in benzyl alcohol detections above the SL is observed starting around 2011.

Increased benzyl alcohol occurrence has not been limited to DMMP projects. A compilation of surface sediment benzyl alcohol data for the Lower Duwamish Waterway shows a dramatic increase in both detection frequency and the frequency of exceedance of the SL in the datasets collected after 2010 (S. McGroddy, Pers. Communication, 2016). Figure 2 summarizes the Lower Duwamish Waterway data.

The DMMP and Lower Duwamish data raise the question: are we really seeing an increase in benzyl alcohol concentrations in Washington State sediments, or could there be other factors at play? To answer this question, Seattle District reached out to local laboratories and consultants familiar with sediment sampling and the analysis of benzyl alcohol in sediments.

#### **Analytical Improvements**

The primary analytical method used to measure benzyl alcohol is EPA Method 8270 for semi-volatile organic compounds. The basic underlying principles (gas chromatography and mass spectrometry) have not changed since DMMP sediment data collection began in earnest in the early 1990s. Historically, benzyl alcohol recoveries have been challenging for laboratories due to chromatographic interferences. In the 1990s, larger volumes of sediment were required for extraction; frequently these extracts contained high levels of humic materials and other interferents that required additional cleanup steps. Any materials that could not be removed could have affected chromatography and, more specifically, could have resulted in non-detect results for more reactive compounds such as benzyl alcohol<sup>1</sup> (S. McGroddy, personal communication, 2016).

Faced with demands for lower detection limits for many of the analytes of EPA Method 8270, laboratories have worked hard to increase the efficiency of their sample extraction and analysis methods including replacing or upgrading instruments, injectors, solvents, extraction procedures, and more. Increased efficiency enables the laboratory to reduce the sample mass required for analysis which is important because it reduces the amount of matrix interference in the sample. The cumulative effect of these numerous individual improvements is likely a contributing factor to the sudden recent increase in both the frequency and magnitude of detections of benzyl alcohol.

A recent (2015) sediment monitoring event at the Boeing Plant 2 Superfund Early Action Site clearly demonstrates the impact of laboratory improvements on analytical results for benzyl alcohol (AMEC, 2015). Benzyl alcohol was not detected in six sediment samples collected at +7 feet MLLW from the recently restored shoreline area at the site. The sample results were rejected due to low (less than 10%)

<sup>&</sup>lt;sup>1</sup> EPA Method 8270D Section 1.4.6 states: "Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material." (EPA, 1998)

Laboratory Control Sample (LCS) recoveries. In response, the laboratory quickly and aggressively tackled the problem with internal extraction and methodological improvements. LCS recoveries were dramatically improved, and re-analysis of the six samples resulted in benzyl alcohol detections in three of the six samples, with a maximum concentration of 360 ug/kg (AMEC, 2015).

Our research into the increase in benzyl alcohol detections suggests that both the increase in frequency of detection of benzyl alcohol and the magnitude of the concentrations reported are due to improvements in analytical technologies and techniques. If this is true, then much of the historical benzyl alcohol data associated with sediment samples in Washington State may underestimate the frequency of detection and concentrations of benzyl alcohol. It is important to keep this caveat in mind when evaluating time trends in the distribution of benzyl alcohol, its co-occurrence with benzoic acid, and benthic toxicity associated with its presence.

#### Sources - Industrial and Natural

Benzyl alcohol is an aromatic organic alcohol produced and used industrially as a solvent, a preservative, and as feedstock for the manufacture of other chemicals. The chemical is commonly used in the soap, perfume and flavoring industries and as an ingredient in ointments and cosmetics; it is also frequently used in inks, paints, epoxy resins and paint strippers (HSDB, 2016; HPD, 2016). Benzyl alcohol is added as a carrier solvent for flavoring substances to some foods and beverages at a level up to 400 mg/kg (EC, 2002). In 2009, the FDA approved a 5% solution for treatment of head lice in patients 6 months of age and older (Concordia Pharmaceuticals, 2013; Buck, 2012; CDC, 2016). At lower concentrations (0.9%), benzyl alcohol is available for use as a bacteriostatic preservative in intravenous solutions (Hospira, 2016; Pediatrics in Review, 1984).

Benzyl alcohol is found naturally in a number of plants, including some edible fruits (up to 5 mg/kg) and in green and black tea (1-30 and 1-15 mg/kg respectively) (EC, 2002). It is also found in daffodils (165-330 mg/kg), hyacinths (64-920 mg/kg), jasmine (120-228 mg/kg), rosemary (7-32 mg/kg), tangerines (1-2 mg/kg), blueberries (0.01-0.08 mg/L in fruit juice).

In addition to improvements in analytical technologies and techniques, it is possible that some of the increase in detected benzyl alcohol in Puget Sound can be explained by a growing use of this chemical in consumer products such as food, cosmetics, solvents, etc. Seattle District attempted to address this possibility, but a significant amount of time and effort would be needed to investigate this question properly.

The available literature regarding natural sources of benzyl alcohol focused exclusively on food and flowers. Nothing was found that provided any insight into natural sources of benzyl alcohol in marine sediments.

While no published scientific literature was found in which plant material from common Northwest species was analyzed for benzyl alcohol, there is strong evidence from a habitat restoration project at Boeing Plant 2 on the Duwamish Waterway. Organic matter approved for use at this project was chemically analyzed. The material was derived from a local source of "dark fines," composed primarily of duff (i.e., leaves, branches, bark and stems from the forest floor) and other organic material cleared from forested areas. In two samples taken from fully-aged and partially-aged stockpiles of these dark

fines, benzyl alcohol concentrations were 3,910 and 450 ug/kg, respectively<sup>2</sup> (Floyd|Snider, 2013). Note that the benzyl alcohol concentration in the fully-aged sample was nearly an order of magnitude greater than that in the partially-aged sample, which may indicate that benzyl alcohol is generated by decaying plant matter.

Circumstantial evidence also exists from the four DMMP projects for which BPJ was used. Visible organic matter (leaves, twigs, roots, etc.) was noted in the core/sample logs for all of these projects. This observation was used as one line of evidence to justify waiving biological testing for these projects.

Based on the evidence in hand, we hypothesize that some or all of the benzyl alcohol found in many sediment samples has its origin in herbaceous or ligneous material from the terrestrial environment.

# **Biodegradation**

Studies using the Organization for Economic Cooperation and Development biodegradation testing protocols has shown that benzyl alcohol is readily biodegradable, with 94% biodegradation measured in a standard 28-day test conducted under aerobic conditions (HSDB, 2016). A shorter 7-day test (also under aerobic conditions) produced the same percentage of biodegradation (92-96%) (HSDB, 2016). If released to water, benzyl alcohol is expected to undergo microbial degradation under aerobic and anaerobic conditions (EPA, 1993; Howard, 1993). Using sediment from an anoxic salt marsh, benzyl alcohol underwent degradation to carbon dioxide and methane after a 2-month incubation period (Howard, 1993).

Biodegradation also occurs readily in wastewater treatment facilities under both aerobic and anaerobic conditions. Benzyl alcohol underwent 70% biological oxygen demand in 5 days under aerobic conditions using an acclimated mixed microbial culture (Howard, 1993). Under anaerobic conditions, benzyl alcohol underwent 100% mineralization within two weeks when inoculated with municipal digester sludge (Howard, 1993). The fraction of benzyl alcohol removed by wastewater treatment plants in the Puget Sound region is unknown. While benzyl alcohol is readily biodegradable, the fraction removed depends on temperature and retention time, among other factors. If benzyl alcohol is not completely removed, it will appear in the effluent discharged to the receiving waters. For example, benzyl alcohol was detected in effluent samples from two of ten treatment plants in Illinois (Ellis, 1982)

Benzoic acid is a degradation product of benzyl alcohol and is structurally very similar. Benzoic acid biodegradability has been extensively studied with study results confirming that it too is readily biodegradable under both aerobic and anaerobic scenarios (HSDB, 2016).

Like benzyl alcohol, benzoic acid has many industrial uses in the preservative and flavor industry (Wibbertmann et al, 2000). It is also on the list of DMMP COCs for marine and freshwater sediments. The marine SL and ML for benzoic acid are 650 and 760 ug/kg, respectively.

Both benzyl alcohol and benzoic acid are of low concern for bioaccumulation. Benzyl alcohol's reported range of octanol-water partitioning coefficients (log  $K_{ow}$ ) is relatively low: 1.00 to 1.16 (EPA, 1978; Montgomery, 2000). The reported range of log  $K_{ow}$  values for benzoic acid is slightly higher: 1.69 to 2.18 (Montgomery, 2000). Chemicals with low octanol-water partitioning coefficients (log  $K_{ow}$  < 2.7)

<sup>&</sup>lt;sup>2</sup> Benzoic acid concentrations were also elevated at 5,600 and 3,630 ug/kg for the fully aged and partially-aged stockpiles, respectively. The DMMP marine SL for benzoic acid is 650 ug/kg.

generally have low soil sorption, low bioaccumulative risk, high biodegradation rate, high solubility and greater mobility (Weiner, 2008).

Our hypothesis is that benzyl alcohol in dredged material disposed at the DMMP open-water sites is biodegraded to benzoic acid within a short time span and poses a low bioaccumulative risk to benthic organisms.

#### **Geographic Distribution**

If common Northwest tree and plant species do contain benzyl alcohol, and debris from these trees and plants is entering marine waters via riverine or other discharges, then this chemical would be expected to be found throughout Puget Sound, including non-urban areas, geographically removed from possible industrial sources or wastewater outfalls. And, since benzyl alcohol is readily biodegraded to benzoic acid, one would expect benzoic acid to co-occur with benzyl alcohol. These hypotheses were investigated by plotting benzyl alcohol and benzoic acid data from Ecology's Environment Information Management (EIM) database using ArcGIS. The time span covered by the data was 1984-2015.

Figures 3a-d show the detected occurrences of benzyl alcohol and benzoic acid in four non-urban embayments. The four embayments shown – Carr Inlet, Dabob Bay, Holmes Harbor and Samish Bay – were used during development of the DMMP dioxin guidelines as non-urban reference areas, and are considered to represent background conditions in Puget Sound. As can be seen from the figures, benzyl alcohol exceeded the DMMP SL in two of the reference embayments (Carr Inlet and Dabob Bay), with concentrations reaching as high as 281 ug/kg. Benzoic acid (BZA) exceeded its marine SL in three of the embayments (Carr Inlet, Dabob Bay and Samish Bay), with concentrations as high as 1,700 ug/kg.

Of note is the fact that benzyl alcohol and benzoic acid detections did not always co-occur in these reference areas. Possible explanations include the complete biodegradation of benzyl alcohol to benzoic acid at those locations where only benzoic acid was detected, or fresh inputs of benzyl alcohol with storm-deposited woody debris at stations where only benzyl alcohol was detected. Another possibility is that the analytical issues referred to earlier in this paper resulted in inaccurate measurements of one or both chemicals. To test this hypothesis, co-occurrence of benzyl alcohol and benzoic acid was examined for data generated in 2011 or later, which presumably was generated using more advanced technologies and techniques than older data. Figure 4 shows detected occurrences of benzyl alcohol and benzoic acid throughout Puget Sound since 2011. Several observations can be made from this figure. First, benzoic acid does co-occur at most stations where benzyl alcohol was detected. Second, benzyl alcohol was detected far less than benzoic acid and always near the shoreline. Third, benzoic acid was much more widely distributed than benzyl alcohol, and in some areas – such as the San Juan Islands and Discovery Bay – was the only one of the two chemicals detected. What this means in terms of sources and relative biodegradation rates of benzyl alcohol and benzoic acid will require additional investigation to understand.

#### **Disposal Site Monitoring Data**

The five non-dispersive DMMP disposal sites (Anderson-Ketron, Commencement Bay, Elliott Bay, Port Gardner, and Bellingham Bay) are monitored periodically to ensure that the DMMP disposal site management objectives are being met. Monitoring includes chemical analysis of sediment samples taken from on-site stations as well as samples taken from perimeter stations located one-eighth of a nautical mile outside of the disposal site boundary. Data from all 19 monitoring studies (DMMP, 2015c) conducted at the non-dispersive sites since establishment of the sites in 1988-89 were reviewed. Benzyl

alcohol was not detected at any of the on-site and perimeter sampling stations during any monitoring event except one. The non-detect reporting limits were below the SL in all cases. In the one study in which benzyl alcohol was detected – Commencement Bay monitoring in 2007 (SAIC, 2008) – the detected concentrations ranged from 4.7 to 21 ug/kg (at 8 stations), which is well below the SL. This finding is important, because it demonstrates that the evaluation procedures used by the DMMP agencies, including the use of BPJ for some projects, has not resulted in on-site benzyl alcohol concentrations exceeding the DMMP SL value (57 ug/kg).

While benzyl alcohol was rarely detected at the disposal sites, benzoic acid was frequently detected. This finding provides further support for the hypothesis that any benzyl alcohol in disposed sediments is rapidly biodegraded to benzoic acid which is more persistent in the marine environment. The last disposal event within a dredging year occurs at or before the end of the in-water work window, which is typically mid-February. Sampling for monitoring studies tends to occur in late spring or early summer. This would leave several months for biodegradation of benzyl alcohol to occur, which could explain why benzyl alcohol is usually not detected at the disposal sites, while benzoic acid is detected. It should be noted that while benzoic acid was found during many of the monitoring studies, it was never detected at concentrations exceeding its marine SL.

It is important to note that the majority of the monitoring data for the disposal sites was generated prior to 2011. Therefore, it is possible these data underestimate the sediment benzyl alcohol concentrations due to the analytical issues discussed earlier.

# **Evaluation of Toxicity**

Our investigation supports the hypotheses that a natural source exists for at least some of the benzyl alcohol found in Puget Sound waters and that, regardless of the source, benzyl alcohol rapidly biodegrades to benzoic acid, which has a much higher SL. Nevertheless, the DMMP agencies agreed that Seattle District should investigate the toxicity of benzyl alcohol to ensure that the disposal site management objective (Site Condition II – minor adverse effects) was not being exceeded, even for short periods, at the disposal sites.

Two lines of investigation were pursued. First, bioassay data from Ecology's EIM, Seattle District's Dredged Analysis Information System (DAIS), and Ecology's Puget Sound Ambient Monitoring Program<sup>3</sup> (PSAMP) database that were associated with detected benzyl alcohol concentrations above the SL were reviewed. Second, a literature review was conducted for ecotoxicity results associated with benzyl alcohol.

#### **Bioassay Data Findings**

The DMMP bioassays include the 10-day amphipod mortality test; 48-hour sediment larval development test; and the 20-day *Neanthes* mortality and growth test. An additional bioassay, the sea urchin fertilization test, has been used in PSAMP. Bioassay data for sediment samples with detected concentrations of benzyl alcohol above the DMMP SL were compiled from several sources in order to assess the relationship between benzyl alcohol concentrations and bioassay results. These included Ecology's EIM system and PSAMP database; Seattle District's DAIS database; and the data report from a Lower Duwamish subsurface investigation conducted in 2012 (USACE, 2013).

<sup>&</sup>lt;sup>3</sup> PSAMP is now known as the Puget Sound Ecosystem Monitoring Program (PSEMP)

Bioassay results were evaluated for two subsets of samples – DMMP and PSAMP. These subsets were evaluated separately because the PSAMP samples were all subjected to the sea urchin fertilization test, while the DMMP samples were subjected only to bioassays used within DMMP. It should be noted that two of the studies (EBCHEM and HYLWD99-1) in the "DMMP" subset were not actually DMMP projects, but were subjected to DMMP bioassays only. Toxicity was evaluated for DMMP samples by comparing bioassay results against the DMMP interpretation guidelines (DMMP, 2015b). For the PSAMP samples, the toxicity interpretations assigned by PSAMP scientists were used. The DMMP samples are discussed first, followed by the PSAMP samples.

The ability to demonstrate sediment toxicity depends on the number of tests being run and the sensitivity of the organisms used. The following sections present the bioassay data available for sediment samples with concentrations of benzyl alcohol exceeding the SL. This dataset is relatively small and for many samples includes only a single bioassay. Therefore, conclusions drawn from an evaluation of the data must be used with some degree of caution.

**DMMP samples**. For marine dredging projects evaluated by the DMMP agencies, two levels of biological response are defined for each bioassay. A "2-hit" response is a minor response. A 2-hit response is required in two or more bioassays in order for the sample to fail biological testing. A "1-hit" response is a higher-intensity response. Only one bioassay needs to exhibit a 1-hit response for a sediment sample to fail biological testing.

DMMP samples with a detected benzyl alcohol concentration greater than the DMMP SL of 57 ug/kg and for which one or more DMMP bioassays were run were compiled. This included 26 samples from six individual studies (Table 1).

Of the 17 samples subjected to the entire suite of DMMP bioassays and passing, the highest concentration of benzyl alcohol was 290 ug/kg (sample LDW18 0-2.8C). For this sample, there was a hit under the 2-hit rule for the larval test, but no corroborating hit in another bioassay. Therefore, this sample passed biological testing. Sample 1C06, with a concentration of 150 ug/kg, exhibited no hits at either hit-level for any of the DMMP bioassays. One sample (EBCHEMEW-12), with a benzyl alcohol concentration of 870 ug/kg, was only subjected to the amphipod test, but exhibited neither a 1-hit nor 2-hit level of response in that bioassay.

The assessment of toxicity potentially attributable to benzyl alcohol was complicated by the fact that many of the samples also had one or more other co-occurring chemicals of concern exceeding SL. Table 2 lists the 10 samples that were subjected to the full suite of DMMP bioassays and for which the only chemical exceeding SL was benzyl alcohol. All 10 samples passed biological testing. There was only one sediment sample that failed bioassay testing for which the only chemical exceeding the screening level was benzyl alcohol. This sample (EBCHEMWW-02) had a benzyl alcohol concentration of 8,800 ug/kg (Table 1), which is two orders of magnitude above the DMMP SL. Only the amphipod test was run on this sample, but it exhibited a hit under the 1-hit rule.

In summary, results from the DMMP samples support the hypothesis that benzyl alcohol alone is not toxic enough to cause DMMP bioassay testing failures at or near the current screening level.

**PSAMP samples**. Table 3 includes all the PSAMP records for which the sea urchin fertilization assay was conducted on samples with detected concentrations of benzyl alcohol above the DMMP SL. Five of the 15 sediment samples listed in Table 3 were also subjected to the amphipod test. The highest

concentration of benzyl alcohol (678 J ug/kg) occurred for sample UWI2007-202, which was found to be non-toxic in the fertilization test.

The three samples that exhibited toxicity in the fertilization test had co-occurring chemicals of concern other than benzyl alcohol that were highly elevated, including phthalates, PAHs, phenolic compounds and dibenzofuran. The one sample that exhibited toxicity in both the fertilization test and the amphipod test had a concentration of bis (2-ethylhexyl) phthalate of 8,300 ug/kg, which is equal to the DMMP maximum level. Due to the multiple SL exceedances associated with cases of demonstrated toxicity in the fertilization test, nothing can be concluded about the contribution of benzyl alcohol to the toxicity observed in these three samples.

The PSAMP sea urchin fertilization data provide further evidence that benzyl alcohol is not likely toxic at the DMMP SL. Concentrations as high as 678 ug/kg were demonstrated to be non-toxic in this test, despite the presence of other COCs.

# **Ecotoxicity Literature Data**

Benzyl alcohol is generally considered to be of relatively low toxicity to humans at low- to moderate-concentrations (HSDB, 2016). In many mammals (including humans), benzyl alcohol is quickly oxidized to benzoic acid, conjugated with the amino acid glycine in the liver, and excreted as hippuric acid. However, this metabolic pathway may not be well developed in premature infants and is thought to be a factor in benzyl alcohol's known toxicity in premature infants (Pediatrics in Review, 1984; HSDB, 2016).

A survey of EPA's online EcoTox database was performed to evaluate the aquatic ecotoxicity of benzyl alcohol. Relevant aquatic toxicity studies for benzyl alcohol are limited to a few primary studies conducted prior to 2000 that exposed test species to various aqueous concentrations of benzyl alcohol. Attachment 1 contains a summary of the findings for studies with defined endpoints such as LC50 or EC50. Benzyl alcohol concentrations for the observed LC, EC, or IC50 endpoints ranged from 10 mg/L (in fish) up to 892 mg/L (protozoa).

Using the aqueous concentrations reported in the literature and the equilibrium partitioning model, the predicted sediment concentration ( $C_{sed}$ ) of a non-ionizable organic compound required to produce the measured aqueous concentration ( $C_w$ ) can be calculated using the following equation:

$$C_{sed} = C_w x (K_{oc} x f_{oc}) x (mg/1,000 ug)$$

Where

 $K_{oc}$  = soil-water partition coefficient in terms of soil organic carbon (L/kg)

 $f_{oc}$  = decimal fraction of organic carbon (unitless)

C<sub>sed</sub> = soil/sediment concentration (ug/kg)

 $C_w$  = aqueous concentration (mg/L)

The above equilibrium partitioning model equation can be used to relate aqueous and bulk sediment concentrations for non-ionic organics. Benzyl alcohol, a weak acid with a pK<sub>a</sub> of 15.4, is expected to behave predominantly as a non-ionic species in the pH range (pH = 8.0 - 8.1) typically encountered in the marine environment. The parameters in the formula were assigned the following values:

 $K_{oc} = 27 \text{ L/kg (Gerstl, } 1990^4)$  $f_{oc} = 0.01 (1\%)$ 

Using the minimum (10 mg/L) and maximum (770 mg/L) effective concentrations for invertebrates and vertebrates in Attachment 1, the calculated equilibrium sediment concentrations are 2,700 ug/kg and 208,000 ug/kg, respectively. The minimum calculated equilibrium sediment concentration (2,700 ug/kg) is nearly two orders of magnitude greater than the current DMMP SL (57 ug/kg) and suggests that the current SL may be overly conservative.

Note that in a sediment-porewater-water column scenario in which the sediment is the assumed primary source of the contaminant to the system, porewater concentrations are expected to exceed water column concentrations. Thus, a higher sediment concentration may be required to produce toxic water column concentrations for the pelagic species listed in Attachment 1.

# Basis of Regulatory Guidelines for Benzyl Alcohol

#### PSDDA/DMMP

Benzyl alcohol was among the COCs for which apparent effects thresholds (AETs) were established in the 1980s to make clean-up decisions for contaminated sediment in Commencement Bay. The database used to develop the AETs was later expanded to include chemical and biological data from areas outside of Commencement Bay. The AETs derived from the larger database became the basis for the PSDDA chemical evaluation guidelines. The AET approach identified concentrations of contaminants that were associated with adverse biological effects. However, the empirical relationships used to establish AETs did not prove a cause-and-effect relationship between contaminants and effects (Tetra Tech, 1986). This was primarily due to the multiple COCs present in sediment samples and the potential for synergistic effects.

The highest AET (HAET) for four biological indicators was used to establish a PSDDA maximum level (ML) for most, but not all, of the COCs. For the majority of the COCs with an ML, the SL was initially set equal to 10% of the ML or to the lowest AET (LAET), whichever was lower. For some chemicals, such as benzyl alcohol, 10% of the ML was lower than the concentration in sediment from a reference area. In those cases, the SL was set equal to the reference concentration. The original SL and ML for benzyl alcohol were 10 and 73 ug/kg respectively (PSDDA, 1988). The 10 ug/kg value likely represented a reporting limit, although documentation for this could not be found. The SL for benzyl alcohol was raised to 25 ug/kg in 1994, likely due to difficulties routinely achieving lower analytical reporting limits. In 1997, the AETs were recalculated and the SL and ML for benzyl alcohol were set at their current concentrations of 57 and 870 ug/kg respectively (DMMP, 1997). The practice of setting the SL equal to 10% of the ML was abandoned at that time and the SL for benzyl alcohol was set equal to the LAET instead. Attachment 2 lists the AETs used to select the current benzyl alcohol SL and ML.

 $<sup>^4</sup>$  Gerstl (1990) reported an empirically derived log  $K_{oc}$  of 1.43 for benzyl alcohol. This was the only empirically-derived log  $K_{oc}$  found in the literature survey. For comparison, the log  $K_{ow}$  for benzyl alcohol in the literature ranges from 1.00 to 1.16 (EPA, 1978; Montgomery, 2000). Using Di Toro's equation (log  $K_{oc}$  = 0.983 log  $K_{ow}$  + 0.00028) for non-ionizable, semivolatile organic compounds and a log  $K_{ow}$  of 1.1 (EPA, 1978), a log  $K_{oc}$  of 1.08 can be computed. This equates to a  $K_{oc}$  of 12.07 L/kg. Using this value for  $K_{oc}$ , calculated sediment concentrations for the range of toxicity concentrations reported in the literature for invertebrates and vertebrates range from 1,200 to 93,900 ug/kg.

#### **SMS**

The State of Washington also adopted the AET approach for development of its Sediment Management Standards (SMS). The SMS rule was originally adopted in 1991, with subsequent amendments in 1995 and 2013. Under the current SMS, the sediment quality standard (SQS) and cleanup screening level (CSL) for benzyl alcohol are 57 and 73 ug/kg respectively (Ecology, 2013). Both the DMMP SL and SMS SQS are set equal to the LAET. However, unlike DMMP, which set the ML equal to the HAET, the CSL was set equal to the second lowest AET.

# The Role of Benzyl Alcohol in Development of the AETs

There is evidence that the early developers of the 1988 AETs were aware that, unlike metals and PAHs, benzyl alcohol was not a major chemical player driving AET sensitivity. Barrick (1988; page 57) states (bold emphasis added):

"The following chemical groups do not <u>uniquely</u> account for predicted impacts for either the amphipod bioassay or benthic infauna AET:

- Miscellaneous organic compounds including pentachlorophenol, resin acids, organic bases (e.g., N-nitrosodiphenylamine), and several Hazardous Substance List compounds including 2-methylnaphthalene, dibenzofuran, benzoic acid, **benzyl alcohol** (low detection limits for the latter two compounds are sometimes difficult to attain but may not be essential)."

#### **Other State and Federal Guidelines**

A survey of other state and federal agency guidelines for the regulation of contaminants in marine sediments indicates that benzyl alcohol appears to be of little or no concern outside of Washington State. Of four states identified with marine sediment quality evaluation criteria (Alaska, California, New York, and Florida), none included a screening level for benzyl alcohol (ADEC, 2001, 2013; NJDEP, 2009, 2015; CDWR, 1995; MacDonald, 1994; NYSDEC, 2014). Among federal agencies, the well-known National Oceanic and Atmospheric Administration (NOAA) Effects Range-Low (ERLs) and Effects Range-Median (ERMs) sediment quality guidelines also do not include values for benzyl alcohol (NOAA, 1999; 2008).

# Summary

In the past few years, the DMMP agencies have seen an increase in the number of projects with detected benzyl alcohol concentrations that exceed the SL. Evidence exists that this phenomenon may be tied to recent improvements in analytical technologies and techniques. Multiple lines of evidence suggest the occurrence of benzyl alcohol is not a significant cause of concern to the DMMP agencies:

- Benzyl alcohol likely occurs naturally in plant-derived material in marine sediment.
- Benzyl alcohol is likely readily biodegraded in the marine environment.
- Benzyl alcohol detections are widespread in Washington State and have been found in both urban and non-urban areas.

- Benzyl alcohol has seldom been detected at the DMMP non-dispersive disposal sites during monitoring<sup>5</sup>.
- Bioassay data indicate that benzyl alcohol has low toxicity.
- Sediment benzyl alcohol concentrations derived from aquatic toxicity data using equilibrium partitioning are more than two orders of magnitude greater than the current SL.

# Proposed Action/Modification

On the basis of the above lines of evidence, the DMMP agencies do not believe that benzyl alcohol is a chemical of significant concern at the concentrations found in many dredging projects. The DMMP agencies recommend re-evaluation of the current SL for benzyl alcohol, including possible recalculation of the AETs or use of other benthic toxicity modeling tools, to update the DMMP evaluation guidelines for this COC. In the meantime, the information presented in this paper will be used to inform any future use of best professional judgment to determine the need for biological testing when benzyl alcohol is the only COC exceeding SL.

# Implication for other DMMP COCs

Other chemicals that are known to occur or are suspected of occurring naturally include benzoic acid, phenol, 2-methylphenol (o-cresol), 4-methylphenol (p-cresol), and 2,4-dimethylphenol. These chemicals have occasionally been the only COCs exceeding SL for DMMP projects but, so far, this has not occurred with the frequency seen for benzyl alcohol. However, given the evidence provided in this paper of the wide distribution of benzoic acid, and detections of benzoic acid in reference embayments at concentrations exceeding the SL, it is very possible that such cases will be encountered in the future, especially for benzoic acid. The DMMP agencies will continue to investigate these COCs to determine the appropriateness of using best professional judgment as has been proposed here for benzyl alcohol. Results of further investigations will be presented in SMARM papers as necessary.

<sup>&</sup>lt;sup>5</sup> Caveat: the majority of the monitoring data for the disposal sites was generated prior to 2011. Therefore, it is possible these data underestimate the sediment benzyl alcohol concentrations due to the analytical issues discussed in this paper.

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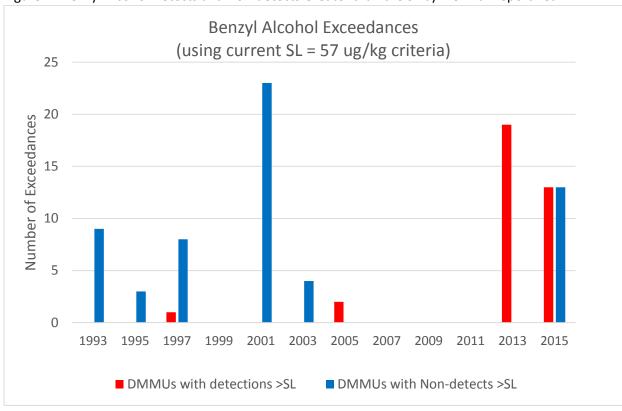
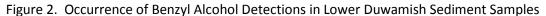
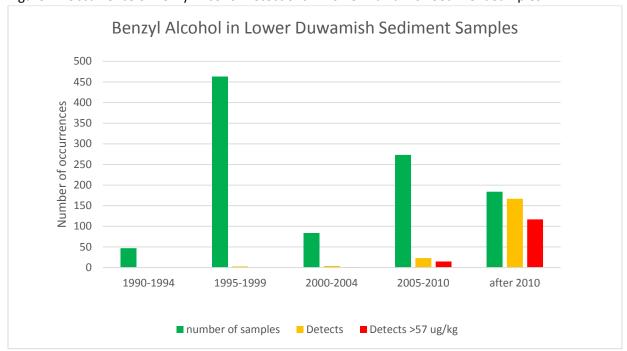


Figure 1. Benzyl Alcohol Detects and Non-detects Greater than the SL by Biennial Report Year





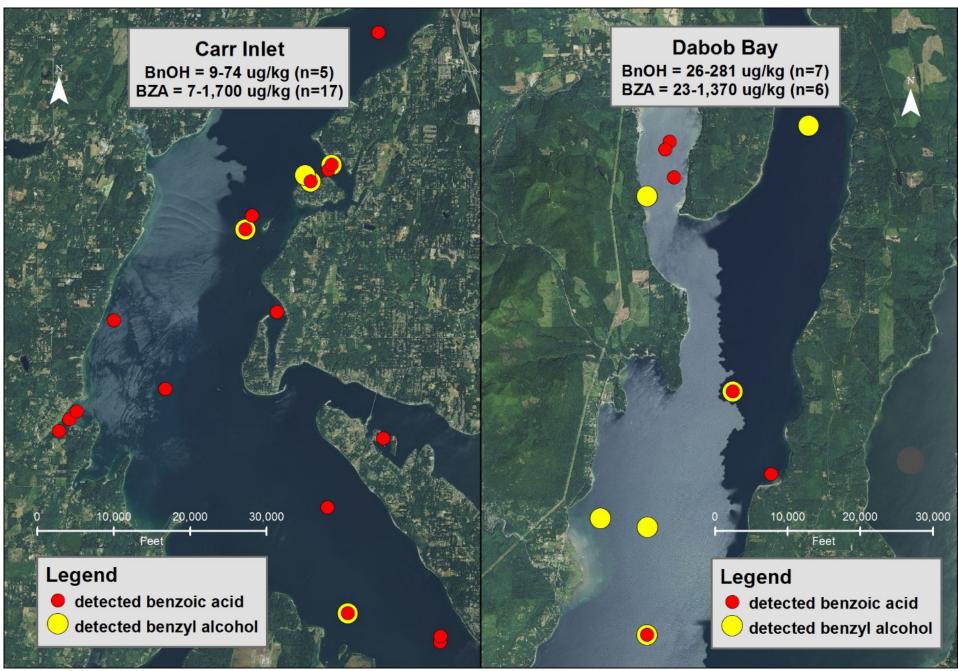


Figure 3a. Detected Benzyl Alcohol and Benzoic Acid in Carr Inlet (data from EIM)

Figure 3b. Detected Benzyl Alcohol and Benzoic Acid in Dabob Bay (data from EIM)

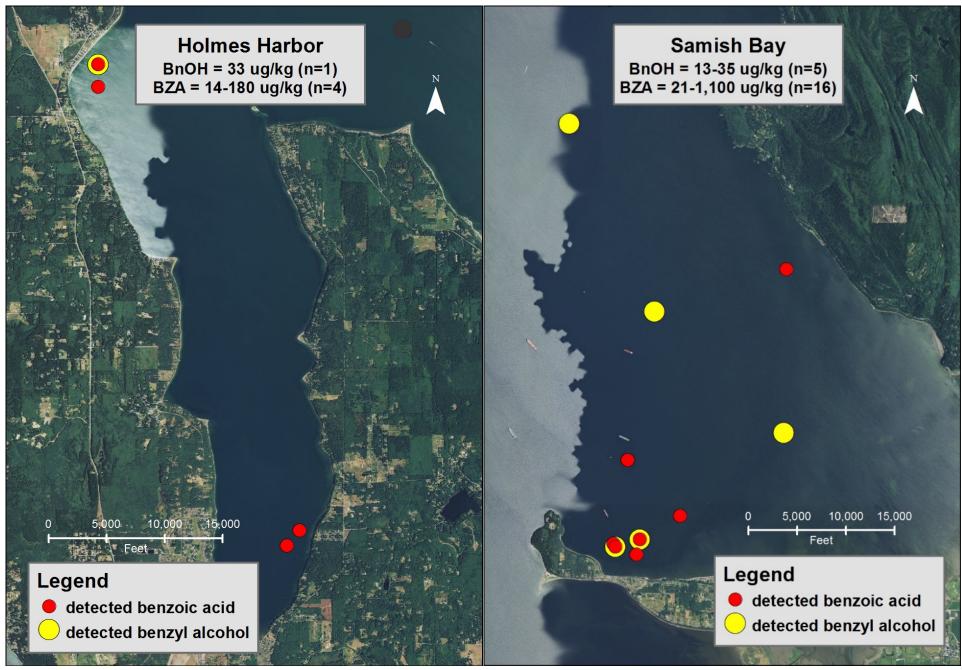


Figure 3c. Detected Benzyl Alcohol and Benzoic Acid in Holmes Harbor (data from EIM) Figure 3d. Detected Benzyl Alcohol and Benzoic Acid in Samish Bay (data from EIM)

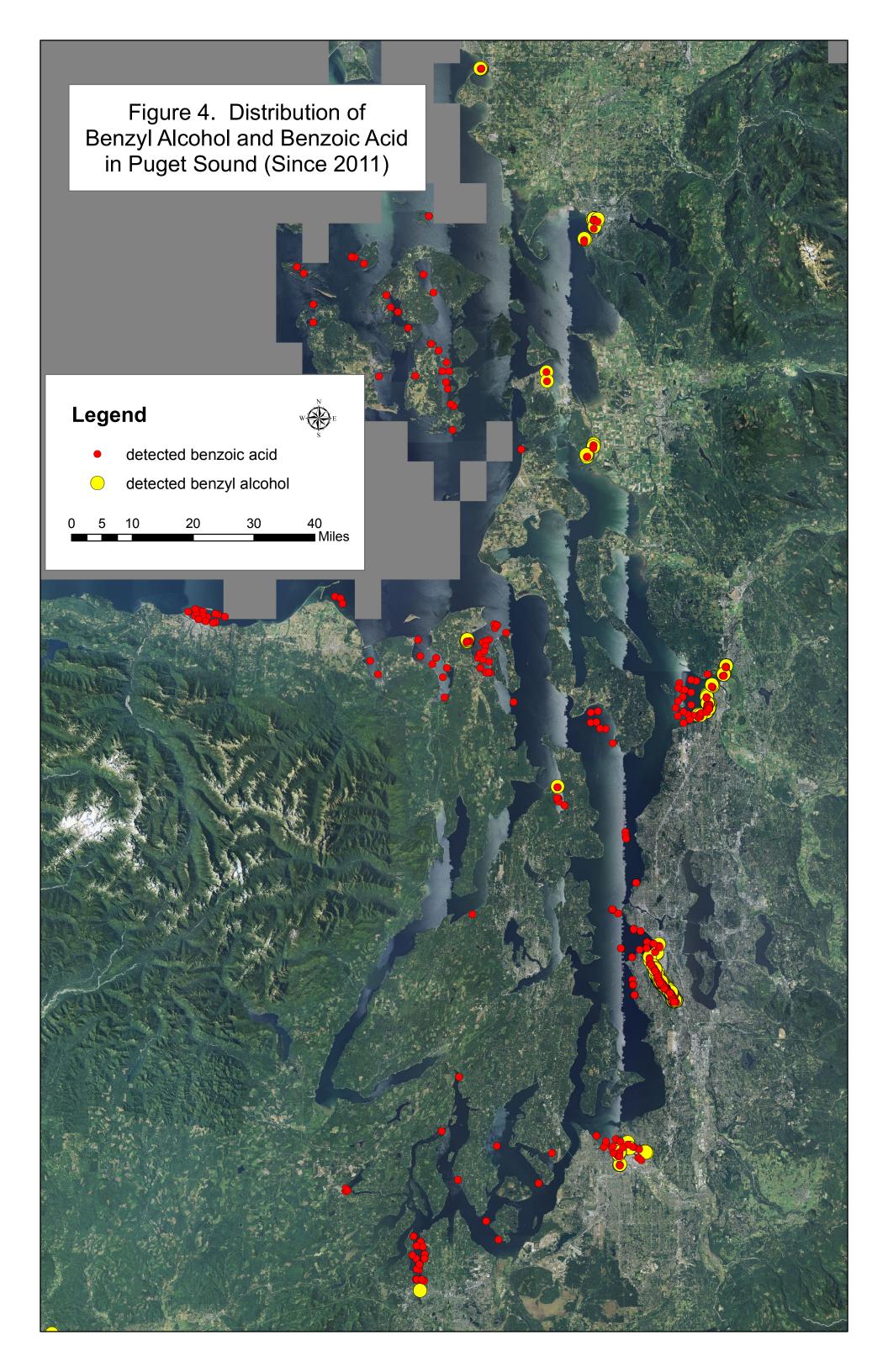


Table 1. DMMP Bioassay Results for Benzyl Alcohol Concentrations Greater than the Screening Level (57 ug/kg)

					Benzyl Alcohol					Overall	Other SL .
	Study_ID	Year	Sample ID	Location	Value (ug/kg)	LQ	Amphipod	Larval	Neanthes	Interpretation	exceedances
-	DUW111BF308	2011	DMMU 4	DNC - Section A	60		Pass	Pass	Pass	Pass	none
-	DUW111BF308	2011	DMMU 12	DNC - Section B	66		Pass	Pass	Pass	Pass	none
-	DUW111BF308	2011	DMMU 17	DNC - Section B	68		Pass	2-hit	Pass	Pass	none
	DUW111BF308	2011	DMMU 11	DNC - Section B	72		Pass	2-hit	Pass	Pass	DDT
	HYLWD99-1	1999	HYLWD99S15	Hylebos Waterway	75	J	no data	Pass	Pass	Pass	BBP, PCBs
	DUW111BF308	2011	DMMU 5	DNC - Section A	82		Pass	2-hit	Pass	Pass	none
	LDSI	2012	LDW07 2-4C2	Lower Duwamish	84		Pass	2-hit	Pass	Pass	PCBs
s A	LDSI	2012	LDW08 0-4C1	Lower Duwamish	84	J	Pass	2-hit	Pass	Pass	PCBs
ssa	DUW111BF308	2011	DMMU 7	DNC - Section A	86		Pass	2-hit	Pass	Pass	none
DMMP bioassays	DUW111BF308	2011	DMMU 10	DNC - Section B	91		Pass	Pass	Pass	Pass	none
₽ Ł	LDSI	2012	LDW09 0-2.1C	Lower Duwamish	120		Pass	2-hit	Pass	Pass	PCBs
Σ	LDSI	2012	LDW11 0-3.2C	Lower Duwamish	130		Pass	2-hit	Pass	Pass	PCBs
of D	DUW111BF308	2011	DMMU 8	DNC - Section B	140		Pass	Pass	Pass	Pass	none
suite	DUW111BF308	2011	DMMU 9	DNC - Section B	140		Pass	Pass	Pass	Pass	none
ns II	PST181BF112	1996	1C06	Seattle Harbor EW	150	D	Pass	Pass	Pass	Pass	TBT, numerous PAHs, dibenzofuran, PCBs
full	DUW111BF308	2011	DMMU 6	DNC - Section A	200		Pass	2-hit	Pass	Pass	none
	LDSI	2012	LDW07 0-2C1	Lower Duwamish	200		Pass	2-hit	Pass	Pass	PCBs
	LDSI	2012	LDW18 0-2.8C	Lower Duwamish	290		Pass	2-hit	Pass	Pass	none
	EWSIA1CF181	2002	S1A-CMP-3	Seattle Harbor EW	92	J	1-hit	Pass	Pass	Fail	Hg, TBT, fluoranthene, pyrene, PCBs
	LDSI	2012	LDW13 2-7.2C2	Lower Duwamish	100		Pass	1-hit	Pass	Fail	PCBs
	LDSI	2012	LDW16 0-2.5C	Lower Duwamish	130		Pass	1-hit	Pass	Fail	PCBs
	LDSI	2012	LDW17 0-3.5C	Lower Duwamish	160		Pass	1-hit	Pass	Fail	PCBs
	EBCHEM	1985	EBCHEMWW-08	Elliott Bay	140	J	2 pass/2 fail <sup>1</sup>	no data	no data	ND	BBP, Hg
pool >	EBCHEM	1985	EBCHEMEW-12	Elliott Bay	870	J	Pass	no data	no data	ND	chrysene
amphipod test only	EBCHEM	1985	EBCHEMSS-03	Elliott Bay	1300	J	1-hit	no data	no data	Fail	numerous metals and PAHs
	EBCHEM	1985	EBCHEMWW-02	Elliott Bay	8800	J	1-hit	no data	no data	Fail	none

 $<sup>^{1}</sup>$ There were four reference sediment samples run. The pass/fail interpretation of this sample depends on which reference it is compared to.

DNC = Duwamish Navigation Channel

LQ = lab qualifier

BBP = butyl benzyl phthalate

EW = East Waterway D = diluted sample Hg = mercury

LDSI = Lower Duwamish Subsurface Investigation

J = estimate

PAHs = polyaromatic hydrocarbons

PCBs = polychlorinated biphenyls

Table 2. Samples Subjected to Full Suite of DMMP Bioassays and for which Benzyl Alcohol was the only SL Exceedance

			Benzyl Alcohol					
Study ID	Year	Sample ID	Value (ug/kg) LQ	Amphipod	Larval	Neanthes	Overall	other SL exceedances
DUW111BF308	2011	DMMU 4	60	Pass	Pass	Pass	Pass	none
DUW111BF308	2011	DMMU 12	66	Pass	Pass	Pass	Pass	none
DUW111BF308	2011	DMMU 17	68	Pass	2-hit	Pass	Pass	none
DUW111BF308	2011	DMMU 5	82	Pass	2-hit	Pass	Pass	none
DUW111BF308	2011	DMMU 7	86	Pass	2-hit	Pass	Pass	none
DUW111BF308	2011	DMMU 10	91	Pass	Pass	Pass	Pass	none
DUW111BF308	2011	DMMU 8	140	Pass	Pass	Pass	Pass	none
DUW111BF308	2011	DMMU 9	140	Pass	Pass	Pass	Pass	none
DUW111BF308	2011	DMMU 6	200	Pass	2-hit	Pass	Pass	none
LDSI	2012	LDW18 0-2.8C	290	Pass	2-hit	Pass	Pass	none

LDSI = Lower Duwamish Subsurface Invest.

LQ = lab qualifier

ug/kg = micrograms/kilograms

Table 3. PSAMP Bioassays

Sample ID	Location	PSAMP stratum	Benzyl Alcohol Value (ug/kg)	LQ	Amphipod (E. estuarius )	sea urchin fertilization	Overall interpretation	other SL exceedances	
UWI2007-183	Elliott Bay, Pier 54	Harbor	58	J	Not Tested	Non-Toxic	Non-Toxic	2,4-dimethylphenol (53 J ug/kg); benzoic acid (1,160 J ug/kg)	
PSAMP_SP-41	Port Angeles	Urban	66	J	Non-Toxic	Non-Toxic	Non-Toxic	phenol (1,230 ug/kg)	
PSAMP_SP-323	Coon Bay	Basin	70	NJ	Not Tested	Non-Toxic	Non-Toxic	benzoic acid (966 J ug/kg)	
PSAMP_SP-55	Possession Sound	Rural	81	J	Not Tested	Non-Toxic	Non-Toxic	2,4-dimethylphenol (39 J ug/kg)	
UWI2010-53	Bellingham Bay	Urban	89	J	Moderate Toxicity	Moderate Toxicity	Moderate Toxicity	bis (2-ethylhexyl) phthalate (8,300 ug/kg)	
PSAMP_SP-177	Discovery Bay	Rural	100	J	Non-Toxic	Non-Toxic	Non-Toxic	none	
PSAMP_SP-405	Boundary Bay	Basin	108	J	Non-Toxic	Non-Toxic	Non-Toxic	2,4-dimethylphenol (86 J ug/kg); 2-methylphenol (76 ug/kg)	
PSAMP_SP-128	Sisters Point	Rural	112	J	Not Tested	Non-Toxic	Non-Toxic	phenol (1,480 ug/kg)	
PSAMP_SP-224	Mosquito Point	Basin	120	J	Not Tested	Non-Toxic	Non-Toxic	di-n-butyl phthalate (1,760 ug/kg); phenol (1,340 ug/kg)	
PSAMP_SP-118	Shoofly Creek	Rural	128	J	Not Tested	Non-Toxic	Non-Toxic	di-n-butyl phthalate (1,980 ug/kg); phenol (1,780 ug/kg)	
PSAMP_SP-83	South Port Townsend	Urban	141	J	Non-Toxic	Non-Toxic	Non-Toxic	phenol (1,200 J ug/kg)	
PSAMP_SP-367	Middle Everett Harbor	Harbor	171	J	Not Tested	High Toxicity	High Toxicity	chrysene (1,910 ug/kg); dibenzofuran (888 ug/kg); fluoranthene (4,300 ug/kg); 2-methylphenol (104 ug/kg); pyrene (3,250 ug/kg)	
PSAMP_SP-96	Sund Creek	Basin	210	J	Not Tested	Moderate Toxicity	Moderate Toxicity	di-n-butyl phthalate (2,990 ug/kg); phenol (1,180 ug/kg)	
UWI2007-203	Duwamish River, North	Harbor	371	J	Not Tested	Non-Toxic	Non-Toxic	2,4-dimethylphenol (181 ug/kg); 2-methylphenol (212 J ug/kg)	
UWI2007-203	Duwamish River, North	Harbor	382	J	Not Tested	Non-Toxic	Non-Toxic	2,4-dimethylphenol (181 ug/kg); 2-methylphenol (212 J ug/kg)	
UWI2007-202	East Waterway, South End	Harbor	678	J	Not Tested	Non-Toxic	Non-Toxic	2,4-dimethylphenol (330 ug/kg); benzoic acid (2,040 J ug/kg); butyl benzyl phthalate (86 J ug/kg); bis (2-ethylhexyl) phthalate (2,150 ug/kg); fluoranthene (1,110 ug/kg); 2-methylphenol (372 J ug/kg); PCBs (574 ug/kg)	

ug/kg = micrograms/kilograms

LQ = lab qualifier

J = estimate

N = there is evidence that the analyte is present in the sample

PCBs = polychlorinated biphenyls

# Attachment 1

# Benzyl Alcohol Aquatic Toxicity Literature Summary Compilation of relevant aquatic toxicity data available from EPA's EcoTox database\*

		Special features	Effect	Endpoint	Effective Concentration Mean	Units	Reference	Notes
Cyanobacteria		· ·		'				
Anabaena inaequalis	blue-green algae			3-h EC50	>100,000	ug/L	Stratton & Corke (1982)	photosynthesis reduction
Anabena variabilis	blue-green algae		Population	2-h EC50	>100,000	ug/L	Stratton & Corke (1982)	photosynthesis reduction
Anabaena cylindrica	blue-green algae			3-h EC50	>100,000	ug/L	Stratton & Corke (1982)	photosynthesis reduction
Algae								
Scenedesmus quadricauda	green algae		Population	3-h EC50	>100,000	ug/L	Stratton & Corke (1982)	
Chlorella pyrenoidosa	green algae		Population	3-h EC50	>100,000	ug/L	Stratton & Corke (1982)	
Protozoa								
Tetrahymena pyriformis	Ciliate	pH 7.35	Population	2-day IC50	891,880	ug/L	Schultz et al (1996)	Cell multiplication inhibition test. Inhibition concentration to 50% of test organisms
				2-day IC50	853,470	ug/L	Schultz et al (1996)	Life stage unknown
Invertebrates: Crustacea								
Daphnia magna	Water flea		Behavior	24-hr EC50	55,000	ug/L	Bringman & Kuhn (1982)	
Vertebrata: Fish								
Pimephales promelas	Flathead minnow	juveniles	Mortality	4-day LC50	460,000	ug/L	Mattson et al (1976)	
		juveniles	Mortality	24-h LC50	770,000	ug/L	Mattson et al (1976)	
		juveniles	Mortality	1-h LC50	770,000	ug/L	Mattson et al (1976)	
		juveniles	Mortality	2-day LC50	770,000	ug/L	Mattson et al (1976)	
		juveniles	Mortality	3-day LC50	480,000	ug/L	Mattson et al (1976)	
			Mortality	45-min LC100	1,050,000	ug/L	Terhaar et al (1972)	100% mortality or 0% survival of organism
Lepomis macrochirus	Bluegill	pH 7.6 - 7.9	Mortality	4-day LC50	10,000	ug/L	Dawson et al (1977)	
Leuciscus idus	Ide		Mortality	LC50	646,000	ug/L	Knie et al (1983)	exposure duration not reported
Menidia beryllina	Inland silverside	pH 7.6 - 7.9	Mortality	4-day LC50	10,000	ug/L	Dawson et al (1977)	

Notes:

\*Accessed February 2016

EC = Effective Concentration

LC = Lethal Concentration

IC = Inhibitory Concentration

Lowest LC50 or EC50 in **bold**.

# **Attachment 2**

# **Benzyl Alcohol AETs**

Gries, 1997 states:

"Agencies are using 1994 amphipod, 1988 benthic, 1986 Microtox, and 1986 oyster AETs to determine LAETs."

	Amphipod	Oyster	Benthic	Microtox
1986 AETs	73	73	73	57
1988 AETs	870	73	870	57
1994 AETs	73	na	na	na

	LAET	HAET	Current SL	Current ML
Benzyl Alcohol	57	870	57	870